

Improved oxidative stability of estolide esters[☆]

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Abstract

Some concerns have been raised regarding the oxidative stability of vegetable-based fluids. Thus, a wide range of commercial and vegetable-based materials were evaluated for their oxidative stability by the rotating bomb oxidative test (RBOT). RBOT values ranged from 13 to 552 min. Two estolides, coconut-oleic estolide 2-ethylhexyl ester (coco) and oleic estolide 2-ethylhexyl ester (oleic), were evaluated for their oxidative stability by RBOT. As in the case with all vegetable oils, an oxidative stability package must be utilized to help decrease their rate of oxidation. A series of formulations were conducted in which the two estolides had an oxidative stability package added prior to the RBOT. In both cases, dramatic increases in the oxidative stability were observed. The coconut-oleic estolide 2-ethylhexyl ester gave the best RBOT values, 504 min with 3.5% oxidative stability package. Both estolides were formulated to meet commercial crankcase requirements (~200 min) with as little as 1.0 and 1.5% oxidative stability package. The viscosity index ranged from 179 to 190 for the oleic estolide 2-ethylhexyl ester, whereas the coconut-oleic estolide 2-ethylhexyl ester had slightly lower viscosity indices ranging from 161 to 174. These two estolide esters have displayed far superior oxidative stability, 504 (coco) and 426 (oleic) min, are of reasonable cost, and were more suitable as a base stock for biodegradable lubricants and functional fluids than current commercial, vegetable-based materials.

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1. Introduction

Estolides are a class of esters based on vegetable oils (Isbell et al., 1994, 2000; Cermak and Isbell, 2001a,c) that form when the carboxylic acid functionality of one fatty acid reacts at the site of unsaturation of another fatty acid to form an ester linkage (Fig. 1). The secondary ester linkages of the estolide are more resistant to hydrolysis than triglycerides and the unique structure of the

[☆] Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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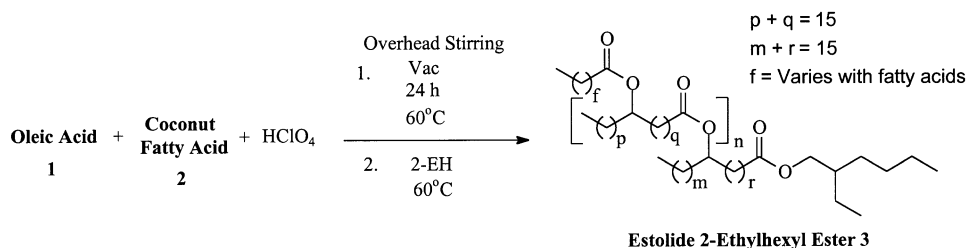


Fig. 1. Reaction scheme for the formation of complex estolide 2-ethylhexyl esters.

estolide results in materials that have far superior physical properties compared with vegetable and mineral oils (Isbell and Cermak, 2000; Cermak and Isbell, 2002).

There are a number of ways that the oxidative stability of an oil may be measured; some common ways are: oxidative stability index (OSI; Akoh, 1994); rotating bomb oxidation test (RBOT) (American Society for Testing Materials, 1998b; Glancey et al., 1998); differential scanning calorimetry (DSC; Bowman and Stachowiak, 1998); Indiana stirring oxidation test (ISOT; Du et al., 2002); and the thin-film microoxidation test (Adhvaryu and Erhan, 2000). Many vegetable-based oils, carbohydrate fatty acid polyesters, and fat substitutes have their oxidative stability measured with the OSI, which is a milder oxidation test than the RBOT. The industry usually dictates the method or instrument to be used for a particular test. Thus, most food applications require the use of the OSI (Frega et al., 1999; Al-Neshawy and Al-Eid, 2000). Most vegetable-based oils that are used in the edible market have not been subjected to the RBOT to date. While the petroleum industry requires a testing with much harsher conditions than the food industry, the RBOT and microoxidation are the recommended tests, because of the environment in which they are used.

A reliable method for following and measuring the stability of a functional fluid is the RBOT, in which a large amount of catalyst is placed with the sample under oxygen pressure (American Society for Testing Materials, 1998b). The bomb is pressurized to 620 kPa with the test material and stirred at 150 °C. The test is complete once the pressure in the bomb drops by 175 kPa after

reaching a maximum pressure, which is designated as the RBOT time, usually reported in minutes.

Some of the concerns with using vegetable-based material are that they have poor oxidative stability (Akoh, 1994; Isbell et al., 1999) as well as below standard cold weather properties (Asadauskas and Erhan, 1999). Because estolides are derived from vegetable oils, they were assumed to have these same undesirable characteristics, but cold weather properties of these estolides turned out to be suprisingly superior than materials currently on the market.

Some concerns have been raised regarding the oxidative stability of vegetable-based functional fluids (Glancey et al., 1998). A functional fluid is any material that may be used in any working device, hydraulic, crankcase, or lubricating fluid to name a few. A number of ways to improve the oxidative stability of an oil, as well as an estolide, exist either through synthetic or oxidative stability improvements. Akoh (1994) reported that refined soybean oil had an OSI (Firestone, 1994), of 9.4 h at 110 °C, but once the oil was partially hydrogenated, the OSI increased to 15.3 h at 110 °C, an improvement of more than 60%. The same approach was taken with the oleic estolides, which underwent hydrogenation with 2% w/w of 10% palladium on activated carbon to obtain completely saturated estolides (Isbell et al., 2001). The saturated, oleic estolides were expected to be more oxidatively stable than the unsaturated estolides by assuming the same trend displayed by soybean oil held true. However, the final product had undesirable cold weather properties that made it useless as a bio-based functional fluid.

Saturated estolides were synthesized to eliminate the poor oxidative stability problem. In a one step

process, an estolide ester was synthesized with excellent physical properties, pour and cloud points, viscosities and oxidative stabilities. These saturated materials retained good pour point properties and had the potential for increased oxidative stability, in addition to reduced production costs and chemical waste (Cermak and Isbell, 2001a,b,c).

Because a detailed study on the oxidative stability of estolides has not been reported, we performed a series of formulation studies to explore the effects on oxidative stability and compare them with the stabilities of commercially available materials. The formulated estolide esters have been found to have superior low temperature, biodegradability, and lubricating properties than commercially available materials.

2. Materials and methods

2.1. Materials

Hexanes, concentrated sulfuric acid (98%), and acetone were purchased from Fisher Scientific Co. (Fairlawn, NJ). Ethanol was purchased from AAPER Alcohol and Chemical Company (Shelbyville, KY). Potassium hydroxide was obtained from J.T. Baker Chemical Co. (Phillipsburg, NJ). Filter paper was obtained from Whatman (Clifton, NJ). The fatty acid methyl ester (FAME) standard mixtures were obtained from Alltech Associates, Inc. (Deerfield, IL). Petroleum oil: Valvoline® 5W-30, 10W-30, 10W-40, 20W-50, SAE-30 and synthetic oil: Castrol Synthetic® 10W-30 were obtained from Wal-Mart Department Store® (Peoria, IL). Soy based oil: Biosoy® and Soylink® were contributed by the University of Northern Iowa (Cedar Falls, IA). Hydraulic fluid: Traveler Premium Universal Hydraulic Fluid® IVG-46 and Traveler All Season Hydraulic Fluid® IVG-46 were obtained from Tractor Supply Company® (Peoria, IL). Meadowfoam oil was supplied by the Fanning Corp. (Chicago, IL). Environlogic 132, 146, 168 were contributed by Terresolve Technologies Ltd. (Eastlake, OH). Aeroshell 15W-50 Aviation oil was contributed by the Central Illinois Aviators (Galesburg, IL).

2.2. Equipment and procedures

2.2.1. Rotating bomb oxidation test

Rotating bomb oxidation determinations were conducted on a RBOT apparatus manufactured by Koehler (Bohemia, NY) using the ASTM Method D 2272-98 (American Society for Testing Materials, 1998b). Prepared estolides, contributed materials, and commercial products were run at 150 °C. Samples were measured to 50.0 ± 0.5 g with 5.0 ml of reagent water added to the sample. The copper catalyst was measured to 3 m and sanded with 220 grit silicone carbide sand paper produced by Abrasive Leaders and Innovators (Fairborn, OH) and was used immediately. The wire was wound to have an outside diameter of 44–48 mm and a weight of 55.6 ± 0.3 g and to a height of 40–42 mm. The bomb was assembled and slowly purged twice with oxygen. The bomb was charged with 90.0 ± 0.5 psi (620 kPa) of oxygen then tested for leaks by immersing in water. The test was complete after the pressure dropped more than 175 kPa below the maximum pressure. All samples were run in duplicate and the average time was reported.

2.2.2. Gas chromatography analysis

Gas chromatography (GC) analysis was performed with a Hewlett–Packard 5890 Series II gas chromatograph (Palo Alto, CA), equipped with a flame-ionization detector and an autosampler/injector. Analyses were conducted on a SP-2380 30 m \times 0.25 mm i.d. column (Supelco, Bellefonte, PA). Saturated C₈–C₃₀ FAMES were used as standards for identifying the fatty acids.

Parameters for SP-2380 analysis were: column flow 3.3 ml/min with helium head pressure of 103 kPa; split ratio 22:1; programmed ramp 75–165 °C at 15 °C/min, 165–185 °C at 7 °C/min, 185 to 265 °C at 15 °C/min, hold 5 min at 265 °C; injector and detector temperatures set at 25 °C. Retention times for eluted peaks: methyl octanate 1.64 min, methyl decanate 2.01 min, methyl laurate 2.70 min, methyl myristate 3.89 min, methyl palmitate 5.77 min, methyl oleate 9.73 min, and hydroxy methyl oleate 19.52 min.

Table 1
RBOT times of various functional fluids

Sample	Average time (min)
Aeroshell® 15W-50 Aviation oil	552
Biosoy®	28
Castrol® synthetic 10W-30	256
Crambe oil ^a	13
Environlogic®-132 Terrsolve	67
Environlogic®-146 Terrsolve	51
Environlogic®-168 Terrsolve	71
Meadowfoam oil ^a -crude	20
Soybean oil ^a	13
Soylink®	83
Traveller® All Season H.F. ^b IVG-46	274
Traveller® Premium Univ. H.F. ^b IVG-46	464
Valvoline® SAE 5W-30	228
Valvoline® SAE 10W-30	223
Valvoline® SAE 10W-40	224
Valvoline® SAE 20W-50	214
Valvoline® SAE 30	224

^a Unformulated, no oxidative stability package.

^b Hydraulic fluid.

viscometer bath set at 40.0 and 100.0 °C. Viscosity and viscosity index were calculated using ASTM methods D 445-97 (American Society for Testing Materials, 1997) and ASTM D 2270-93 (American Society for Testing Materials, 1998a), respectively. All viscosity measurements were run in duplicate and the average value was reported.

2.2.5. GC analysis of hydroxy fatty acids

Analytical estolide samples for GC were prepared by heating a 10 mg sample of estolide or estolide 2-ethylhexyl ester in 0.5 ml of 0.5 M KOH/MeOH to reflux on a heating block for 60 min in a sealed vial. After cooling to room temperature, 2 ml of 1 M H₂SO₄/MeOH was added to the vial, the vial was resealed, and heated to reflux on a heating block for 30 min. The solution was transferred to a separatory funnel with water (1 ml) and washed with hexanes (2 × 2 ml), dried over sodium sulfate, gravity filtered, placed in a GC vial with hexanes, sealed, and injected into the GC.

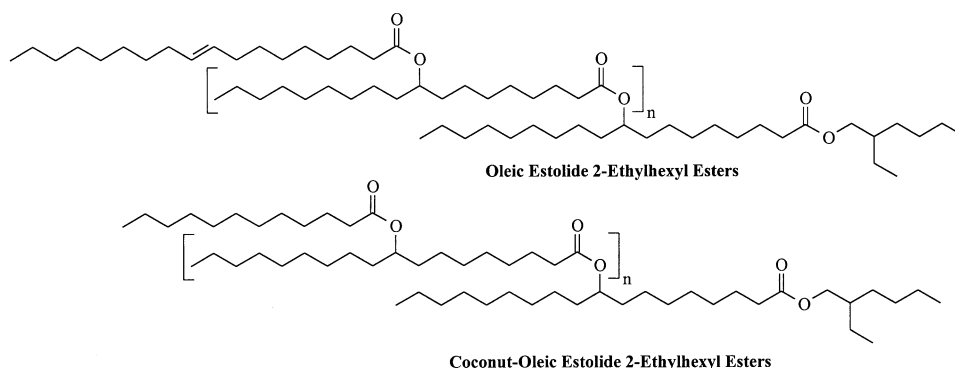


Fig. 2. Chemical formula for oleic estolide 2-ethylhexyl ester and coconut-oleic estolide 2-ethylhexyl ester.

2.2.3. Iodine values and estolide number

Iodine values (IV) were calculated from the GC results using AOCS Method Cd 1c-85 (Firestone, 1994).

2.2.4. Viscosity

Viscosity measurements were made using calibrated Cannon–Fenske viscometer tubes purchased from Cannon Instrument Co. (State College, PA). Viscosity measurements were made in a Temp-Trol (Precision Scientific, Chicago, IL)

3. Results and discussion

The rotation bomb oxidation test (RBOT) times were determined on a wide range of petroleum, vegetable-based, and synthetic materials at 150 °C and these results are listed in Table 1. Of the materials tested, the materials formulated with some sort of oxidative stability package performed best. The normal petroleum and synthetic motor oils had acceptable RBOT times greater than 200 min, whereas a premium hydraulic fluid had a

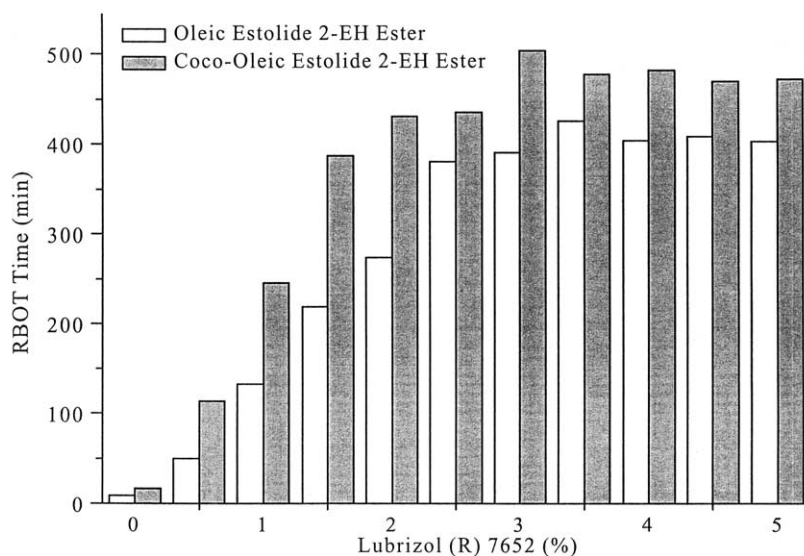


Fig. 3. RBOT time vs. the amount of oxidative stability additive package.

Table 2

RBOT times and viscosity properties of oleic estolide 2-ethylhexyl esters with varying amounts of Lubrizol (R) 7652 additive

Sample	Additive (%) ^a	Average RBOT time (min)	Viscosity @ 40 °C (cSt)	Viscosity @ 100 °C (cSt)	Viscosity index
O-1	0.0	8.5	41.6	8.6	190
O-2	0.5	50	41.5	8.5	188
O-3	1.0	132	41.4	8.5	187
O-4	1.5	219	41.1	8.5	188
O-5	2.0	274	41.1	8.4	186
O-6	2.5	381	41.0	8.4	186
O-7	3.0	390	41.1	8.4	186
O-8	3.5	426	41.2	8.4	185
O-9	4.0	404	41.4	8.4	183
O-10	4.5	408	41.0	8.3	184
O-11	5.0	402	40.7	8.3	185
O-12	7.0	372	40.8	8.2	181
O-13	10.0	279	40.2	8.0	179
O-14	100.0	29	25.6	4.3	52

^a Lubrizol (R) 7652.

RBOT time greater than 400 min. The best performing material (Table 1) was a mid-cost, aviation oil used for single engine, propeller planes with a RBOT time of 552 min. All of the vegetable-based oils were unformulated and had very low RBOT times, usually 20 min or less. Even crude Meadowfoam oil, *Limnanthes alba*, which is the most oxidatively stable, crude vegetable oil

(Isbell et al., 1999) with an OSI of about 247 h, had an RBOT time of only 20 min. This example demonstrates the harsh conditions that the RBOT exerted on the fluids being tested. Other bio-based materials listed in Table 1 had RBOT times of less than 100 min. The average RBOT times for these types of fluids are between 55 and 80 min. The two soybean-based materials were formulated with at

Table 3

RBOT times and viscosity properties of coconut-oleic estolide 2-ethylhexyl esters with varying amounts of Lubrizol (R) 7652 additive

Sample	Additive (%) ^a	Average RBOT time (min)	Viscosity @ 40 °C (cSt)	Viscosity @ 100 °C (cSt)	Viscosity index
CO-1	0.0	17	66.5	11.4	166
CO-2	0.5	113	65.7	11.5	172
CO-3	1.0	245	65.9	11.6	171
CO-4	1.5	387	65.4	11.6	173
CO-5	2.0	431	66.0	11.5	170
CO-6	2.5	436	65.5	11.4	169
CO-7	3.0	504	65.0	11.3	168
CO-8	3.5	477	64.5	11.4	169
CO-9	4.0	482	62.5	11.2	174
CO-10	4.5	469	64.3	11.2	168
CO-11	5.0	472	62.8	11.0	168
CO-12	7.0	393	62.8	10.9	165
CO-13	10.0	292	62.1	10.6	161
CO-14	100.0	29	25.64	4.32	52

^a Lubrizol (R) 7652.

least 40–60% additives to make them perform at a marketable level. Akoh (1994) and Isbell et al. (1999) demonstrated that the unsaturation of soybean-based oils has a destructive effect on oxidative stability. Thus, Biosoy, a soybean derivative, had the lowest RBOT time of all the formulated materials tested at 28 min.

Two different estolide 2-ethylhexyl esters were synthesized from oleic acid, Fig. 2 (Isbell et al., 1994) and another was synthesized from oleic and coconut fatty acids, Fig. 2, (Cermak and Isbell, 2003) with 0.05 mol equivalents of perchloric acid at 60 °C under vacuum followed by direct conversion to the corresponding ester by the addition of 2-ethylhexanol at 60 °C for 2 h under vacuum (Fig. 1). The two different estolide 2-ethylhexyl esters were vacuum distilled to remove any excess 2-ethylhexanol, whereas the coconut-oleic estolide 2-ethylhexyl ester underwent additional vacuum distillation to remove any excess fatty acids, thus improving the cloud point of the material (Cermak and Isbell, 2002).

RBOT times were determined on the oleic estolide 2-ethylhexyl ester at 150 °C while varying the amounts of an oxidative stability package, Lubrizol (R) 7652 (Table 2). The unformulated oleic estolide 2-ethylhexyl ester showed an expected low RBOT time of 8.5 min, as was typical for vegetable oils (Table 1). The oxidative stability

package, Lubrizol (R) 7652, is added in 0.5% units based on weight. As 0.5% of the oxidative stability package was added, there was a five times improvement in the RBOT value to 50 min. Addition of a 1.5% oxidative stability package produced an RBOT value of 219 min for the simple oleic estolide, which was comparable with the petroleum crankcase fluids (Table 1). This was an improvement of more than 25 times over the original stability time. The RBOT values reach a maximum with the 3.5% oxidative stability package, which produced a time of 426 min. This time compared favorably with most premium, petroleum hydraulic fluids (Table 1). At this point, any additional oxidative stability package, 4.0–10.0%, showed a destructive effect on the overall RBOT values (Table 2 and Fig. 3).

The viscosities of the formulated oils ranged from 41.6 to 40.2 cSt at 40 °C and 8.6 to 8.0 cSt at 100 °C. In both cases, the viscosities decreased as the amount of the oxidative stability package increased, resulting in viscosity indices from 190 to 179.

The RBOT times were determined on the coconut-oleic estolide 2-ethylhexyl ester, Fig. 2, with varying amounts of an oxidative stability package, Lubrizol (R) 7652, at 150 °C (Table 3 and Fig. 3). The unformulated coconut-oleic estolide 2-ethylhexyl ester showed an expected low RBOT time of

17 min (Table 3). In this case, the coconut-oleic estolide had RBOT values almost two times that of the oleic estolides. This could be accounted for in terms of IV. The simple oleic estolide had an IV of about 40, whereas the coconut-oleic estolide had an IV of about 15. Oxidative stability is known to be readily dependent on the amount of unsaturation in a molecule (Isbell et al., 1999).

The oxidative stability package, Lubrizol (R) 7652, was added in 0.5% units based on the weight of coconut-oleic estolide 2-ethylhexyl ester. As 0.5% of the oxidative stability package was added, there was a 6.5 times improvement in the RBOT value to 113 min. By adding 1.0% oxidative stability package, the RBOT time was increased to 245 min, which exceeds the times for the petroleum crankcase oils listed in Table 1. Therefore, an RBOT time of 200 min, common for most petroleum crankcase oils, could be achieved easily with less than 1.0% oxidative stability package. The coconut-oleic estolide showed that it could be easily and inexpensively formulated into a crankcase formulation.

After adding 2.0% oxidative stability package, the reported RBOT values were similar to that of premium hydraulic fluids. The RBOT values reached a maximum with about 3.0% oxidative stability package that produced an RBOT time of 504 min and compares favorably with aviation oil for single-engine, propeller planes (Table 1), and an improvement of more than 30 times over the original. At this point, as in the oleic estolide case, any additional oxidative stability package, 3.5 to 10.0%, showed a destructive effect on the overall RBOT values (Table 3).

The viscosities of these formulated packages ranged from 66.5 to 62.1 cSt at 40 °C and 11.6 to 10.6 cSt at 100 °C. In both cases, the general trend was that the viscosities decreased as the amount of the oxidative stability package increased, producing viscosity indices from 174 to 161.

The RBOT value of the oleic estolide 2-ethylhexyl ester and the coconut-oleic estolide 2-ethylhexyl ester as the percent of Lubrizol (R) 7652 were not the same. There is a noticeable difference between the two samples tested, as the coconut-oleic estolide 2-ethylhexyl ester gave longer RBOT times for all the data points collected. The most

noticeable case was with the 1.5% oxidative stability package, where the coconut-oleic estolide 2-ethylhexyl ester had almost twice the RBOT value of the oleic estolide 2-ethylhexyl ester. In both cases, the materials showed that they peak at 2.5 and 3.0% and hold somewhat steady as they start to decline in RBOT time with increased oxidative stability package.

4. Conclusions

Both the coconut-oleic estolide 2-ethylhexyl ester and oleic estolide 2-ethylhexyl ester had higher RBOT values than common vegetable-based materials (Table 1). The coconut-oleic estolide 2-ethylhexyl ester had outstanding RBOT values due to the fact that the estolide was “capped” (Cermak and Isbell, 2001c) with saturated fatty acids. As the estolide had fewer degrees of unsaturation incorporated, the RBOT values increased. Thus, the coconut-oleic estolide 2-ethylhexyl ester displayed the best RBOT values and competed favorably with aviation oil as the top commercial performer.

Both the coconut-oleic estolide 2-ethylhexyl ester and oleic estolide 2-ethylhexyl ester have the potential as a functional fluid. Only a small addition of a oxidative stability package made it possible for these esters to meet the oxidative requirements and stabilities of commercial materials as well as outperformed these same products. Also, these estolide esters have excellent low temperature properties where pour points are –33 °C without any additional cold weather formulations.

These two different estolides have many superior physical properties and require only a small amount of additives to improve their oxidative stability. This translates into a potential functional fluid with properties better than current commercial products at a reasonable cost.

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